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# THE SCIENTIFIC MONTHLY

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## THE HISTORY OF CHEMISTRY\*

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CHEMISTRY is the science of the ultimate composition and constitution of matter, of the mutual reaction between two or more substances, and of the influence of factors such as change of temperature, pressure, or extent of surface upon the stability of a substance and its relation to other substances. The chemist studies the great diversity of substances, organic and inorganic, which we see around us; he analyzes these substances, ascertains their composition, and builds them up again from their components; he investigates their behavior with respect to change in external conditions and in relation to other substances. He learns how, not merely to imitate a substance occurring naturally, but to make the identical material artificially and to discover new substances superior in usefulness to those found in nature; and he considers how useful substances may be produced more economically from the raw materials available. The study of chemistry is slowly yielding information as to the nature of biological processes of importance to every one and so is assisting to retain health and to control disease. Indeed our material well-being and comfort depend in large part upon a fundamental knowledge of chemical processes and how to control them; and continued progress along these lines will be limited only by the rate at which we extend our knowledge of fundamentals, what chemistry has achieved being but a fraction of what it may do for us.

The great practical achievements of chemistry are comparatively recent, almost entirely within the last sixty years, quite largely indeed within the present century. They are so manifold that it would not be feasible in the space allotted even to mention a fraction of them; consequently I have endeavored only to sketch in general outline, as free from technicalities as possible, the development of the main funda-

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mental principles of chemistry, and even in this have been forced to omit much that is important.

#### DEVELOPMENT OF THE IDEA OF CHEMICAL ELEMENTS AND OF THEIR MUTUAL RELATIONSHIP

Two hundred years ago, at which time the classical mathematics had already reached a high state of development, chemistry had not begun to be a science, nor even an art; it was more or less of a mystery, in which language was used to conceal the fact that there was no thought—as it still is used by some today. Boyle in “The Sceptical Chymist,” first published in 1661, refers to the vagueness of the ideas then current in the following terms:<sup>1</sup>

The confidence wherewith chymists are wont to call each of the substances we speak of by the name of sulphur or mercury, or the other of the hypostatical principles, and the intolerable ambiguity they allow themselves in their writings and expressions, makes it necessary for me . . . . to complain of the unreasonable liberty they give themselves of playing with names at pleasure . . . . I cannot but take notice, that the descriptions they give us of that principle or ingredient of mixt bodies, are so intricate, that even those that have endeavored to polish and illustrate the notions of the chymists, are fain to confess that they know not what to make of it either by ingenuous acknowledgments, or descriptions that are not intelligible . . . . Chymists write thus darkly, not because they think their notions too precious to be explained, but because they fear that if they were explained, men would discern, that they are far from being precious. And, indeed, I fear that the chief reason why chymists have written so obscurely of their three principles, may be, that not having clear and distinct notions of them themselves, they cannot write otherwise than confusedly of what they but confusedly apprehend; not to say that divers of them, being conscious to the invalidity of their doctrine, might well enough discern that they could scarce keep themselves from being confuted, but by keeping themselves from being clearly understood . . . . If judicious men, skilled in chymical affairs, shall agree to write clearly and plainly of them, and thereby keep men from being stunned, as it were, or imposed upon by dark and empty words; it is to be hoped, that these (other) men finding, that they can no longer write impertinently and absurdly, without being laughed at for doing so, will be reduced either to write nothing, or books, that may teach us something, and not rob men, as formerly, of invaluable time; and so ceasing to trouble the world with riddles or impertinencies, we shall either by their books receive an advantage, or by their silence escape an inconvenience.

And again,<sup>2</sup> showing that he had no great opinion of their methods:

Methinks the Chymists, in their searches after truth, are not unlike the navigators of Solomon's Tarshish fleet, who brought home from their long and tedious voyages, not only gold, and silver, and ivory, but apes and peacocks too: for so the writings of several (for I say not, all) of your hermetick philosophers present us, together with divers substantial and noble experiments, theories, which either like peacock's feathers make a great

<sup>1</sup>The Sceptical Chymist, Everyman's Edition, pp. 113-6.

<sup>2</sup>Op. cit. p. 227.

show, but are neither solid nor useful; or else like apes, if they have some appearance of being rational, are blemished with some absurdity or other, that when they are attentively considered, make them appear ridiculous.

The general belief of the alchemists appears to have been that there is a primordial matter which, when combined with more or less of one or more of their four so-called elements or principles—fire, air, earth and water—becomes apparent to our senses as the various substances we know; in other words, that matter is the carrier or embodiment of certain qualities which can by appropriate treatment be enhanced or attenuated. It is juster to look upon the alchemists' so-called elements as qualities—such as hotness, coldness, dryness, wetness—typified by the things named, though no single quality would suffice for a single element, as each alchemist tended to endow his elements with such attributes as suited his immediate purpose. In addition to these four elements some made use also of the "hypostatical" (fundamental) principles—salt, sulphur and mercury, which again may be interpreted as typifying fixity in the fire or incombustibility, combustibility, volatility and metallic lustre, respectively. Such views lead one directly to believe in the possibility of transmutation, of changing base metal into gold; for to achieve this, it would be necessary only to effect a suitable change in the proportions of the elemental qualities, a possibility which therefore seemed far from hopeless or absurd.

It is clear that no great progress in chemistry as a science could have been made, so long as such false views prevailed. And indeed the alchemists contributed nothing to the real philosophy of chemistry, although they did discover—by chance, more or less—a few useful substances, such as sulphuric acid (oil of vitrol) and tartar emetic, some of which found application as drugs. For one of the tasks they set for themselves was to find the elixir of youth, a quest along with which went a belief in the efficacy of doses of the strangest mixtures; indeed, an ingenuous person examining the present-day official pharmacopeias might well be led to think that the alchemists continued to flourish and to be powerful until very recent times.

The overthrow of this false philosophy was begun by Robert Boyle, in his "Sceptical Chymist." He endeavored to distinguish the qualities of a substance from its composition, and enunciated views with reference to the difference between elements and compounds which are still held. Thus he writes: "I must not look upon any body as a true principle or element, but as yet compounded, which is not perfectly homogeneous, but is further resolvable into any number of distinct substances, how small soever." "I mean by elements, as those chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called

perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved."<sup>3</sup>

It is difficult to picture the exact status of knowledge of chemical art at that period, partly because the alchemists commonly described their experiments in vague terms, partly because their false theories prevented them from discovering all the pertinent facts and led them to misinterpret much of what they did observe. For instance, the doctrine of the indestructibility of matter—that the total weight of a system remains unaffected by chemical changes taking place within it—now regarded as axiomatic, was not definitely formulated; the material nature of air had not yet been recognized, nor had gases been really differentiated; the process of combustion was not understood, and analytical methods hardly existed.

Boyle's views gained ground very slowly, but the progress of chemistry was hindered for a century by a false theory, the so-called phlogiston theory. According to this view, there is an inflammable principle—phlogiston—which escapes when a substance is burned. For instance, when a metal is burned, phlogiston escapes and a calx or earth remains; on which basis the metal is a compound of calx plus phlogiston, whence it would follow that in order to regenerate the metal, phlogiston must be supplied to the calx by heating with some substance (such as carbon) rich in phlogiston. This theory emphasized the fundamental similarity of all combustion processes, and to that extent was a good and useful hypothesis; but the picture it presented is almost the exact inverse of the real facts, for we now know that a metal in burning actually unites with oxygen, that the calx or oxide weighs more than the metal, and that the system as a whole has lost energy, mainly in the form of heat—all of these changes having to be reversed in order to regenerate the metal from the oxide. The phlogiston theory, despite its falsity, continued to prevail for a century, during which time it befogged the whole subject and paralyzed the advance of chemical philosophy; the net result being that, until nearly the end of the eighteenth century, the subject was as little clear as it had been a hundred years before, although it had in the meantime been enriched by many new observations of importance, and progress along experimental lines had been quickened by improved technique. This prevalence of a false theory, which hindered progress so greatly, leads one to wonder if some of the hypotheses now commonly accepted do not have a similar inverse relation to the real facts, as was the case with the phlogiston theory; it is this type of question which the promoters of the theory of relativity are in effect asking with respect to our fundamental physical ideas.

Another mistaken notion was the material nature of heat. The fact

<sup>3</sup>Op. cit. p. 187.

that flames issue from burning bodies led to the view that they were material objects; and so fire was regarded as one of the elements. Even after the overthrow of the ancient ideas of combustion, it was believed that heat, or caloric as they termed it, though devoid of weight, was a substance—an imponderable, in the same category as light and electricity.

Thus, even as late as 1848, in a very interesting "Manual of Chemistry"<sup>4</sup> the author writes:

The first part comprehends an account of the nature and properties of Heat, Light and Electricity—agents so diffusive and subtle that the common attributes of matter can not be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of Imponderables. They cannot be confined and exhibited in a mass like other bodies, they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them are exactly such as might have been anticipated on the supposition of their materiality. It hence follows that we need only regard them as subtle species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general.

From this it is apparent that the author did not feel quite sure of his ground although Rumford's experiments in 1798 had shown that heat could be generated without limit by friction alone; indeed the question was not determined until the experimental investigations of Joule, published 1843-9, established the doctrine of the conservation of energy, that heat and work are mutually and quantitatively interconvertible.

Thus, up to nearly the close of the 18th century chemistry had not become a science. No descriptions had yet been given which correlated change of properties with change of composition in such a way as to indicate new lines of investigation. Indeed the conception of chemical composition, as we now understand it, had not taken form, because the phenomena—and in particular, the change of weight—accompanying the transformation of one substance into another had not been accurately observed. From this period date the use of the balance, perhaps the most characteristic single tool of the scientific chemist, and the quantitative analysis of chemical changes; and with this advance chemistry begins to be a science, with a growing body of definite principles.

<sup>4</sup>"Manual of Chemistry on the Basis of Dr. Turner's Elements of Chemistry," by John Johnston (1806-79) Professor of Natural Science in the Wesleyan University; new edition, Philadelphia, 1848; p. xiii.

In rendering chemistry a science many men bore a part, but the outstanding figure is Lavoisier, born in 1743, beheaded in 1794 because "the Republic has no need of scientists," a view which, though still widely held implicitly, is not now carried to its logical conclusion in the same way as it was then. Lavoisier's "*Traité élémentaire de chimie*," published in 1789, is a systematic treatise which transformed the subject. He gave a definite meaning to the expression, "chemical composition"; and recognized that the quantity of matter is the same at the end as at the beginning of every operation. He stated that the object of chemistry is "to decompose the different natural bodies, and . . . . . to examine separately the different substances which enter into their combination. We cannot be certain that what we think today to be simple is indeed simple; all we may say is, that such or such a substance is the actual term whereat chemical analysis has arrived, and that with our present knowledge we are unable to subdivide further." This quotation shows that Lavoisier had a much better philosophic attitude towards the whole matter than have had many of the chemists since his time; indeed until recently chemists were so much occupied in accumulating observations that they were prone to neglect the philosophy by means of which alone these multitudinous observations can be correlated.

Lavoisier gave a table of elements, containing thirty-three names, of which twenty-three are still regarded as elements—the definition of a chemical element being that it is a substance which we have not succeeded in breaking up into anything simpler, the atoms of the several chemical elements therefore being, so to speak, the small pieces of tile of different kinds out of which are built up all of the numberless patterns or mosaics which we see about us as diverse kinds of matter. Of the others, five—lime, magnesia, baryta, alumina, silica—are oxides which, with the experimental means then available to Lavoisier, could not be decomposed. These twenty-three elements, the number known at the end of the eighteenth century, comprise the following: carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur; antimony, arsenic, bismuth, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, nickel, platinum, silver, tin, tungsten, zinc. This list, it will be noted, includes only six non-metals, one of which—sulphur—was known to the ancients though not recognized by them as an element in the modern sense of the term. Of the seventeen metals on Lavoisier's list, seven—gold, silver, copper, iron, mercury, lead, tin—were known to the ancients, though not as elements; most of the others were isolated for the first time during the second half of the eighteenth century. Incidentally it may be mentioned, as an illustration of the slowness with which knowledge is applied, that some of these metals—notably, tungsten, molybdenum and manganese—were not used technically for

more than a hundred years after their discovery; we now value them highly, as their use enables us to achieve results of the greatest importance technically and therefore economically, results which otherwise were unattainable. It is of interest, furthermore, to note that the names of two of these elements—cobalt and nickel—derive from words meaning “the devil,” ores of copper admixed with these metals being then considered useless; indeed we have only learned to make use of such ores comparatively recently. Nickel has been produced on a large scale for a short time, and no large use has yet been made of cobalt, although it is comparatively plentiful.

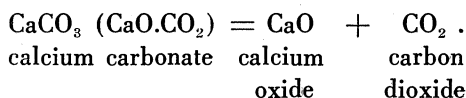
By the year 1800, twenty-seven chemical elements had been recognized, the four added since Lavoisier being uranium, titanium, chromium and tellurium; thirty years later, in 1830, this number had been doubled. The discovery of many of these elements (for instance, the metals associated with platinum—palladium, rhodium, iridium, osmium) was brought about by the application of more and more careful analytical methods, in the hands of men such as Wollaston and Berzelius—the latter alone adding five to the list. The isolation of others, notably the alkali and alkaline earth metals, (potassium, sodium, calcium, strontium, barium) by Davy in 1807, was achieved by a new and powerful method of analysis, namely, the application of the electric current to the breaking up of substances. Davy, after proving definitely by this means that water is composed solely of hydrogen and oxygen, established the fact, surmised by Lavoisier, that the alkalis are oxides of metals; therefore that oxygen, the acid producer as it had been named (erroneously as we now know), is a constituent of the alkalies. He was, however, puzzled by ammonia and in particular by the ammonium radicle or grouping<sup>6</sup> which in its salts resembles so closely the alkali metals; and this puzzle was not solved until about 1840, by which time the idea of the existence of similar compound radicles in organic chemistry was beginning to find general acceptance.

From this period dates the usefulness of the atomic theory, first clearly enunciated by John Dalton in his “New System of Chemical Philosophy” published in 1808. The speculation that matter is ultimately composed of discrete particles, or atoms, had been common in philosophical writings; but it had led to no real progress of knowledge until Dalton showed how the assumption that each element is made up of atoms serves to correlate experimental observations and to suggest new inquiries. On this basis, the myriad substances we see about us are all made up of combinations of a small integral number of atoms of the several elements present, the atoms of each element having characteristic properties, and in particular a characteristic weight. Chemical combination of one element with another is the union of an

<sup>6</sup>See *infra*.



atom of one element with an atom, or a small number of atoms, of the other; this number, in compounds of two elements, seldom exceeds four and is always less than eight, and it is in no wise arbitrary but in accordance with what is now termed the relative valence of the two elements. As a simple case, in the ordinary combustion of carbon (coal) one carbon atom unites with two oxygen atoms, resulting in the formation of carbonic acid gas; or, as the chemist writes it in his shorthand,  $C + O_2 = CO_2$ . In more complicated structures, the number of elements present may be greater than two, but is seldom greater than five; the total number of atoms making up the structure characteristic of the substance is in some cases large, but in all cases it can be pictured as made up of a number of groupings, each composed of two elements. As a simple familiar instance, limestone ( $CaCO_3$ ) is made up of equivalent amounts of lime ( $CaO$ ) and carbonic acid ( $CO_2$ ), and is decomposed into these two proximate constituents in the operation of lime-burning, thus:



Furthermore the lime, when used as mortar, is slowly reconverted into the carbonate by the action of the carbonic acid always present in the atmosphere. In many chemical processes we are dealing with an exchange of partners, the substances A B and C D becoming A D and B C; for example, hydrochloric (muriatic) acid added to a solution of silver nitrate (lunar caustic) yields nitric acid and silver chloride, the latter appearing as an insoluble white curdy substance; or in symbols,  $HCl + AgNO_3 = HNO_3 + AgCl$ . This illustrates the fact that the apparent affinity of one kind of atom for another is not the same under all circumstances, and that consequently a firm and long-standing union of two atoms may be broken up by the entrance of a third under appropriate conditions.

The atomic theory was a very great step in advance, establishing, as it did, the laws and processes of chemistry on a quantitative basis. Progress since Dalton's time has only served to confirm the essential correctness of the atomic theory; indeed there is now no longer need to call it a theory, for the reality of atoms is no more open to question than that of any other fact of physical science. The atoms are infinitesimally small, so small that, if a drop of water were magnified to the size of the earth, the constituent atoms would be about the size of footballs. Perhaps a more striking illustration is that, if the particles in a cubic inch of air were magnified until they would just pass through a very fine sieve (100 meshes to the inch), this fine sand of particles would suffice to cover a highway extending from New York to San Francisco, and one mile wide, with a layer about two feet deep.

We cannot see the actual atoms, it is true, but we can weigh them and measure them and study their characteristics; the same holds true for electricity, which, it may be remarked, is, according to modern views, also made up of units, named electrons, which bear an extraordinarily intimate relation to the structure of the atom itself.

In 1830, as noted above, about fifty-five chemical elements had been recognized, and these include all—with one notable exception, argon, to which we shall refer later—which have yet been found in appreciable quantities in the surface crust of the earth. Since that time the number of recognized elements has been increased by about thirty, most of which, however, are so very rare that only a few grams of them have ever been isolated—in other words, most of them are chemical curiosities kept in small tubes in museums. Indeed the recognition and isolation of the majority of these elements has been possible only through the discovery, about 1860, of the possibility of spectrum analysis. This elegant method depends upon the fact that each chemical element, whether in combination or free, gives, when viewed under appropriate conditions, a so-called spectrum made up of a series of bright lines, the positions, or colors, of which are absolutely characteristic. This method of identification is so sensitive that an element can be recognized even when it is present only in very small amount—an amount of the order of one-millionth of a gram; it therefore enables one to learn how to segregate or concentrate an element originally present in such small quantities that no ordinary chemical test would then suffice to detect it. Likewise, by observation and measurement of the spectra of the sun and stars, it has been definitely determined that the elements present in their upper layers are identical with those which make up the crust of the earth and are already familiar to us, with one or two possible exceptions.

In 1868 Lockyer, while examining the solar spectrum, observed a bright line which did not correspond to any element then known, and attributed it to a hypothetical element helium. This element was not recognized on the earth for about thirty years, although Hillebrand had in the meantime, while examining the mineral uraninite, had some in his hands, but, by reason of its inertness, considered it to be merely nitrogen. It was identified by Rayleigh and Ramsay in the course of their investigation of the inert gases of the atmosphere, an investigation which arose out of the observation—originally made, in a sense, by Cavendish, a century earlier—that there is a fractional difference in density between nitrogen prepared chemically and that obtained from purified air by removal of the oxygen. This investigation resulted in the discovery of a family of five new inert gaseous elements, all of which are present in the atmosphere, argon to the extent of about one percent. by volume, helium and the others in the proportion of a few

parts per million. Argon, therefore, although all around us in enormous quantities—within a house 33 x 33 x 33 feet there is about a ton of air and consequently some forty pounds or 10,000 litres (400 cubic feet) of argon—was not recognized, by reason of its inertness; for neither it, nor any of the argon group, has hitherto been made to enter into chemical combination. But this very inertness is now being taken advantage of; in the case of argon, as a filling for electric light bulbs; in the case of helium, as a non-inflammable filling for balloons, a matter which, during the war, was considered so important that large quantities of it were finally separated from natural gas in Texas, after many difficulties and at very large expense. Incidentally, this is an excellent illustration of the results which may follow from scientific work carried on merely to learn about things, and not with any idea of discovering something of particular use; for the possibility of producing helium on a large scale is a direct outcome of careful observations of the spectrum of various samples of natural gas.

But the greatest interest in helium, from a scientific point of view at least, is in quite another direction, namely, its intimate connection with the phenomenon of radio-activity, or better, with the disintegration of the so-called radio-elements. These radio-elements, the best known of which is radium, first discovered in 1898, differ from the other chemical elements in one respect, but that one very significant, in that they are disintegrating before our eyes. This disintegration, which proceeds at a rate unaffected by any change of temperature or by anything tried hitherto, is accompanied by a continuous emission of energy—a million times greater than is liberated in any change of matter previously known—largely in the form of material particles shot out with great velocity. This energy is so great that one can indeed count the number of particles shot out by observing the flash produced by the bombardment of a suitable screen, as in the spinthariscopes, or the luminous watch dial in which the light is the aggregate of the flashes produced by a quantity of radium which weighs only a millionth of a gram. This phenomenon enables us to detect the presence of a small number of *atoms* of a radio-element; whereas the smallest number of atoms of an element which it has been possible to detect by means of the spectroscope or by the most delicate methods of chemical analysis is at least  $10^{12}$ , a number the magnitude of which will be more obvious from the statement that it is several hundred times the total present human population of the world. It is now definitely established that these material particles are helium atoms, and that this disintegration of the radio-elements is an actual transmutation, a transmutation, however, beyond our present powers to control. If we should ever learn to control this atomic disintegration, it would effect a much greater revolution than was caused by the utilization of coal for power; for in that

case the energy derivable from the atomic disintegration of a shovelful of material would be as great as that now derivable from a thousand tons of coal—in other words we would then be possessed of limitless stores of energy. This has not been done yet, it may not be achieved for a long time, it may not be possible; but he would be a rash man who would deny its possibility. The phenomenon of radio-activity is a very striking illustration of the way in which a new method, a new tool of research, may open up a field which otherwise we would not even sense—nay, hardly be bold enough to imagine; and there is absolutely no reason for believing that other equally novel and unsuspected discoveries will not be made in the future.

From the fact that the material particles shot out by a disintegrating radio-element are helium atoms, it would appear that the helium atom is one of the kinds of brick which go to make up the more complex type of structure of the atoms of the heavier elements. Now the two simplest and lightest atoms known are the hydrogen atom and the helium atom; and there is ground for believing that the hydrogen atom also is one of the bricks of the atom-builder. Indeed recent experiments of Rutherford (1920) indicate that he has succeeded, by bombarding nitrogen atoms with helium atoms, in dislodging hydrogen atoms from somewhere—presumably from the nitrogen atom. If this is confirmed, we shall have to introduce an interpretative reservation into the present definition of an element, according to which a chemical element is a substance not yet resolved into something simpler. This however, is hardly part of the *history* of chemistry; though, one may ask, what is the use of history, beyond being a sort of literary exercise, if it does not enable us to make general predictions as to what is going to happen, for then only will it be a science.

The deduction from experimental evidence that the hydrogen and the helium atom are two of the building bricks brings us back to a very old idea, to the idea that matter as we see it or—one would now say preferably,—the chemical elements are made up of one, two, or at most a few, kinds of primordial stuff. The relative weight of the atoms of the several elements can be determined by simple experiments; these atomic weights were usually referred to hydrogen as unity, hydrogen being the lightest known element, but for practical reasons are now referred to oxygen = 16.00, there being only a fractional difference between these two standards of reference. It was early observed that a much larger proportion of these atomic weights approximate to whole numbers than can be accounted for on the theory of chances. From this it was inferred that the hydrogen atom was this ultimate unit; but there were a number of well established marked exceptions<sup>7</sup> which would not be explained away and so tended to discredit the doctrine. Nevertheless this hypothesis, often called Prout's hypothesis, continued

to be a useful one, as it was the occasion of much of the best work on atomic weights; and in spite of the exceptions, it persisted as an aspiration which was rewarded in time by the discovery of the periodic law of the chemical elements, established by the writings of Mendeleeff.

According to this great generalization "The properties of the elements, and, therefore, the properties of the simple, and of the compound bodies formed from them, are in periodic dependence on their atomic weights." In other words, if the elements are arranged in order of increasing atomic weight, we find that like properties recur regularly, and that by this means like elements are brought together into natural groups, e. g. the alkali metals, the halogens, the inert gases. This periodic classification had a profound effect in leading us toward the correct value of atomic weight of many elements; and in enabling predictions to be made as to the existence and properties of undiscovered elements, predictions which were completely verified in three cases by the subsequent discovery and investigation of the properties and relations of scandium, gallium and germanium. But to record all the consequences of this periodic law would be to recount the achievements in inorganic chemistry in the fifty years elapsed since its discovery; suffice it to say that it forced the chemist to cease thinking about the elements as unrelated entities and instead, to consider them as members of a family or, at the least, as members of a series of related families.

Time has only served to corroborate the essential correctness and usefulness of the periodic classification of the chemical elements; and no evidence has been more conclusive than that derived, within the last few years, from investigations of X-rays and of radio-activity. This work has led to the conception of a characteristic atomic number which changes by unity in passing from one element to its neighbor in the periodic system. It appears indeed that this atomic number is really more fundamental than the atomic weight, that all the properties of an atom, save mass and radio-activity, depend upon the atomic number, which is the number of negative electrons (i. e. atoms of electricity) surrounding the positive nucleus at which the mass of the atom is assumed to be concentrated; or rather, that the distribution of the negative electrons on which the ordinary physical and chemical properties depend is a function, and a periodic function, of the units of electric charge on the nucleus, and hence of the atomic number. It is believed that the lightest known element hydrogen has an atomic number of 1, helium of 2, lithium of 3, and so on up to thorium and uranium, the

<sup>7</sup>These are now showing signs of yielding, in that the elements in question seem to be mixtures of so-called isotopes which have identical chemical properties, and so can not be separated by chemical means, but differ slightly in characteristic weight.

heaviest known elements, with atomic numbers of 91 and 92 respectively. If these views should be confirmed—and their success in correlating diverse phenomena makes it certain that the picture they present is one aspect of reality—we shall have nearly returned to the hypothesis of a primordial stuff; for present evidence indicates that the positive nuclei of hydrogen and helium and the negative electron are amongst the units from which the atoms of the elements are built. But this again is history in the making.

From the considerations just outlined it appears that all of the chemical elements as we know them are of a similar order of complexity, since they belong to a series of families; and consequently that any means which will decompose one element will also decompose others. Moreover, the sequence of atomic numbers indicates that only five elements are missing in the series up to uranium, the heaviest element now known and the parent of one of the two series of radio-active elements. Whether elements heavier than uranium exist is open to question; if they do exist, they would presumably be radio-active, and with a shorter life than uranium. The most common elements in and about the surface layers of the earth are in general elements of smaller atomic number, as is shown by an estimate of the percentage of the several elements which go to make up the earth's "crust," defined for this purpose as a layer ten miles in thickness.

It appears that two elements, oxygen and silicon—the latter wholly in primary combination with the former, the remainder of the oxygen being combined with the other elements—together constitute three-quarters of the earth's crust; and that the eight most abundant elements make up nearly 99 per cent. of the whole.

It is also noteworthy that, of the metals in daily and common use, only aluminum, iron, manganese, chromium, vanadium, and nickel, appear among those elements that are present in the rocks of the crust in sufficient amount to be commonly determinable by the usual processes of analysis. Such common and "every-day" metals as copper, zinc, lead, tin, mercury, silver, gold, and platinum, antimony, arsenic, and bismuth—metals that are of the utmost importance to our civilization and our daily needs—all these are to be found in igneous rocks, if at all, only in scarcely detectable amounts. Though they are ultimately derived from the igneous rocks, they are made available for our use only by processes of concentration into so-called ore bodies.<sup>8</sup>

Up to the present, then, the number of known chemical elements is, excluding the isotopic radio-elements, about eighty. That is, chemists, in spite of laborious and prolonged efforts, analyzing all manner of material from all quarters of the globe—and even from the heavens in the form of meteorites—have been able to resolve their multitudinous diversity into combinations and permutations of some eighty substances; and these hitherto irreducible minima—the so-called chemical

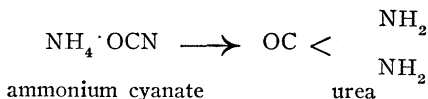
<sup>8</sup>H. S. Washington, J. Franklin Institute, Dec., 1920, p. 778.

elements—are members of a family, or of a group of families, and so represent the same stage of simplicity or complexity of structure. Knowledge of the structure of the atom is extending rapidly, but it would lead too far afield to go into this absorbing question here.

#### DEVELOPMENT OF IDEAS RESPECTING CHEMICAL COMBINATION, PARTICULARLY IN ORGANIC CHEMISTRY

The chemical elements are not all of the same degree of importance to us, although there are not very many which we could well do without; but there are four, in a sense, of supreme importance, as they are the main constituents of all living matter. These four elements are carbon, hydrogen, oxygen, nitrogen, with which are associated relatively small, but absolutely indispensable, proportions of other elements. For a long time it was thought that the substances which make up living matter—the so-called organic compounds—were associated with some sort of vital force, and so were to be placed in another category from mineral substances—the inorganic compounds. But this distinction was broken down, for the first time, nearly one hundred years ago; it remains now only in the names organic and inorganic chemistry, the term organic chemistry now connoting merely the chemistry of carbon compounds, from whatever source derived.

So long as the idea persisted that the behavior of organic substances is determined more or less by a mysterious vital force, progress, it is obvious, could hardly be rapid; and indeed the rise of organic chemistry as a science may be said to date from Wöhler's discovery, in 1828, that urea—a typical product of the animal organism—could be made from materials classed as inorganic compounds. Under certain conditions, the molecule<sup>9</sup> of ammonium cyanate, which is a compound of the ammonium radicle ( $\text{NH}_4$ ) with the cyanate radicle ( $\text{CNO}$ ), undergoes a rearrangement, a change of grouping, yielding urea; or as we would now symbolise it



Here we have, therefore, two different substances composed of the same atoms, and convertible one into another by appropriate treatment; this instance illustrates the fact that the properties of a compound de-

<sup>9</sup>The molecule may be defined, for our present purpose, as the smallest portion of a compound which can be conceived to exist alone; for subdivision if it were carried further, would break up the compound into its constituent parts. The radicle is a grouping of elements, which reacts as a unit and is like a chemical element in many respects, with the outstanding difference that the radicle can, by appropriate treatment, be decomposed into its elements or altered.

pend, not only upon the kinds of atoms and number of each present, but also upon the *arrangement* of these atoms within the molecule. In other words, the behavior of a substance is dependent upon its constitution, just as the behavior of an animal is dependent upon its constitution. But this is to anticipate by some thirty years; for at that time chemists were still a long way from a clear understanding of the matter. The primary reason was a confusion between the atomic weight and the combining weight to be assigned to an element; this confusion resulted in a lack of consistency in assigning formulae to substances—for instance water was then frequently written HO—a circumstance which in turn, so to speak, hid the simple relations of the several compounds and, indeed, makes it hard for us now to follow much of the writing on chemistry at that time. But it would lead too far into a field of interest only to the chemist, to recount the various steps in the slow advance towards an attainment of consistent ideas of chemical combination and constitution. We can only mention some of the outstanding figures in this advance: Wöhler and Liebig, with their discovery (1832) of the radicle benzoyl; Dumas, with his older type theory (1839), Gerhardt and Williamson with modified theories of types of formulation of organic compounds.

Liebig's name cannot however be passed over without mention of the enormous influence which he and his teaching had upon the development of the subject. Shortly after becoming professor at Giessen in 1824 he instituted systematic laboratory instruction in chemistry, and Giessen soon became the most famous chemical school in the world, attracting many who were subsequently themselves to become leaders in further development. Still more important was Liebig's pioneer work on the chemistry of the processes of life, both animal and vegetable, work which makes him the real founder of two branches of the subject—biochemistry and the chemistry of agriculture; the development of these two branches is being attended with incalculable benefits to human welfare.

From about 1830 onwards, interest in chemistry enhanced steadily, the number of competent workers grew rapidly, and there was a constantly increasing body of facts of observation; but these various observations and the deductions from them awaited reconciliation and interpretation which came only when the proper theory was developed. This did not happen until 1860 when, at a conference which had been called in the hope of bringing about some more general understanding of the questions at issue, Carrizzaro brought to the attention of the chemical world the hypothesis of Avogadro, showed how on this basis the apparent anomalies disappear, and so clarified the whole situation. Indeed it may be said that modern chemistry dates from 1860, with the enunciation of clear and consistent views with respect to chemical com-



bination, as a direct consequence of grasping the real significance of Avogadro's hypothesis.

From the gas-laws of Boyle and Gay-Lussac—namely, that equal changes in pressure and in temperature occasion equal changes in equal volumes of gases—and from Gay-Lussac's discovery (1809), that two gases reacting with one another do so in simple proportions by volume and that the volume of the product, when gaseous, also bears a simple relation to that of the factors,—reasoning from these Avogadro about 1811 was led to the hypothesis: Under the same conditions of temperature and pressure, equal volumes of gases contain equal numbers of molecules. The molecule is the smallest particle of a substance obtainable by *mechanical* subdivision; the atom can be obtained only by *chemical* subdivision of the molecule of which it constitutes a part, and is therefore a particle usually incapable of persisting alone but in most cases existing only in combination with other atoms. This combination may be between like atoms, in which case the molecule so formed is that of the element itself, or between unlike atoms, constituting the molecule of a compound. In either case the same principle holds; with the obvious deduction, as Avogadro showed, that the relative weight of two species of gaseous molecules is measured by the ratio of the weights of equal volumes, under the same conditions of temperature and pressure,—i. e. of the densities—of the two gases. A molecule of the elements which are gaseous under ordinary conditions is made up of two atoms, with exception of the family of rare inert gases which are mono-atomic; that of other elements,—for example, sulphur—may contain six or more; in all cases there is, as we now know, a progressive dissociation of the molecules with increasing temperature and diminishing pressure, so that at the highest temperatures and lowest pressures a large proportion of the molecules are in effect broken up into mono-atomic particles.

With the acceptance of Avogadro's hypothesis, the chemist had at last a definite criterion for deciding when he was dealing with really comparable quantities of elements or of compounds; he was enabled to fix the atomic weight definitely, and hence to deduce the correct empirical formula of his compounds. When this was done, many things became clear. For instance, the full significance of the idea underlying the theories of radicles and types, which had been developing for the previous twenty or thirty years, became apparent; and this, in turn, led to the conception of valence, according to which the atom of each element has a maximum saturation capacity with respect to other atoms.

Certain groupings of atoms are so relatively stable that they remain in combination although chemical change is effected in the molecule as a whole; such groupings, known as radicles, react commonly as units and are therefore in many respects analogous to chemical elements, the

chief differences being that the radicle cannot commonly be isolated as such and that it can, of course, be decomposed into its constituent elements. The earliest clear example is the ammonium radicle ( $\text{NH}_4$ ) which forms a whole series of salts differing no more from the corresponding salts of potassium (K) and sodium (Na) than these differ from one another; in other words,  $\text{NH}_4$  can, in principle, replace K or Na in a whole series of compounds each of which closely resembles its analogue. Likewise we have a whole series of organic radicles, ranging from the simplest—methyl ( $\text{CH}_3$ ), ethyl ( $\text{C}_2\text{H}_5$  or  $\text{CH}_3\cdot\text{CH}_2$ )—up to quite complex groupings,—such as stearyl ( $\text{C}_{17}\text{H}_{35}\text{CO}$  or  $\text{CH}_3\cdot(\text{CH}_2)_{16}\text{CO}$ ) but all ideally reducible to a small number of types. For instance, consider the following series of compounds, with the corresponding analogues in which hydrogen (H) is substituted for methyl ( $\text{CH}_3$ ):

$\text{CH}_3\cdot\text{H}$ methane, the main constituent of natural gas	$\text{H}\cdot\text{H}$ hydrogen gas
$\text{CH}_3\cdot\text{OH}$ methyl alcohol	$\text{H}\cdot\text{OH}$ water
$\text{CH}_3\cdot\text{Cl}$ methyl chloride	$\text{H}\cdot\text{Cl}$ hydrochloric acid
$\text{CH}_3\cdot\text{CHO}$ acetaldehyde	$\text{H}\cdot\text{CHO}$ formaldehyde (formalin)
$\text{CH}_3\cdot\text{COOH}$ acetic acid (vinegar)	$\text{H}\cdot\text{COOH}$ formic acid
$(\text{CH}_3)_2\text{O}$ methyl ether	$\text{H}_2\text{O}$ water
$(\text{CH}_3)_2\text{S}$ methyl sulphide	$\text{H}_2\text{S}$ hydrogen sulphide

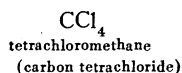
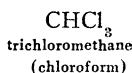
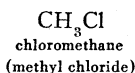
This list could be extended indefinitely, in either direction; for a whole series of other radicles can be regarded as derived from methyl by successive substitution in place of one or more of its H atoms, of  $\text{CH}_3$  groups or chlorine atoms or indeed of any other atom or radicle which exhibits the appropriate affinity relations. For instance, we have:

$\text{CH}_2\cdot\text{H}$ $\text{CH}_3$ methyl	$\text{CH}_2\cdot\text{CH}_3$ $\text{C}_2\text{H}_5$ ethyl	$\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ $\text{C}_3\text{H}_7$ propyl	$\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ $\text{C}_4\text{H}_9$ butyl
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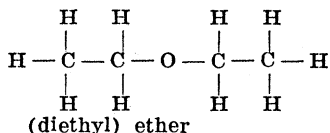
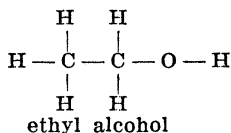
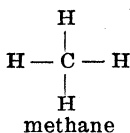
and so on, in homologous series, as it is termed; further  $\text{C}_2\text{H}_4\text{Cl}$ , chlorethyl as in  $(\text{C}_2\text{H}_4\text{Cl})_2\text{S}$ , dichlorethylsulphide (mustard gas);  $\text{CCl}_3$ , trichloromethyl, as in  $\text{CCl}_3\cdot\text{CHO}$ , trichloraldehyde (chloral), and so on.

With the recognition of the relationships just outlined, of the existence of radicles related to one another in a simple manner and of the fact that the multifarious compounds are formed by the possible combinations of the several radicles and elements, it became possible to organize a consistent nomenclature. The advantage of this is obvious; for if to each chemical compound had been assigned an arbitrary name (as has been the case in naming minerals) it would have been possible to read chemical literature only by memorizing a list numbered now in hundreds of thousands—a task which would have been harder than learning the Chinese characters, and would have resulted in a similar retardation of progress. For certain common substances or common

groupings specific names are retained, but in general the name is designed to exhibit the constitution—and therefore the general properties and behavior—of the substance with the least possible memory work; and the chemist gets from these names, in some cases apparently very complicated—e. g. phenyl-dimethyl-isopyrazolone (antipyrin), dimethyl-methane-diethyl-sulphone (sulphonal)—much more information about the substance than the layman gathers from the term “third assistant secretary to the fourth assistant postmaster-general” with respect to the real function of that personage. As simple examples of systematic naming, consider the substances obtainable by chlorinating methane:



Closely allied to the doctrine of radicles and types is the doctrine of valency, according to which each element has a maximum saturation capacity with respect to other elements. This doctrine developed about the same time, though in somewhat more rigid form than would now be generally accepted. Accordingly, to carbon was assigned the valence 4, to oxygen 2, to hydrogen and chlorine 1, and so on; and it was but a short transition to picture the valence numbers as the number of linkings or bonds with which one atom may hold others, and from this to the writing of graphic or structural formulæ. The graphic formula enabled the organic chemist to represent still more satisfactorily the structure of his substances, and has been an indispensable tool in the subsequent great development of organic chemistry; the following simple examples will suffice:

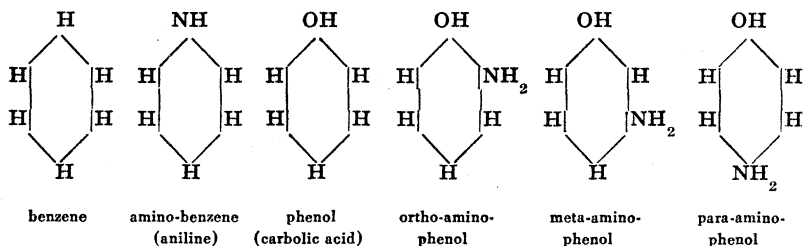


In 1861 appeared the first portion of Kékulé's great text-book which emphasized and illustrated the new views with hundreds of examples. The foundations of modern organic chemistry were therein laid and, what is more important for us here, the date marks the time when the great contribution of organic chemistry to the historical development of the science as a whole was fully rendered.<sup>10</sup>

So far we have mentioned only compounds whose structure can be represented by a straight chain of carbon atoms, and grouped under the general name of aliphatic (or fatty) compounds from the circumstance that fats belong to this category. But there is another category, the so-called aromatic compounds, the simplest, and typical member of which is benzene, which has the empirical formula  $\text{C}_6\text{H}_6$ . A satisfactory structural formula for this substance was first given, in 1865,

<sup>10</sup>F. J. Moore, *History of Chemistry*, p. 173.

by Kékulé who assumed that the six carbon atoms are arranged in a ring, a single hydrogen being attached to each; and all the subsequent work on aromatic compounds has only served to confirm the usefulness of this hypothesis. One instance only can be mentioned here, namely, that whereas there is only one mono-substitution product, (i. e. where one atom of hydrogen is replaced by a different atom or group, as in phenol) there are three disubstitution products (designated as ortho, meta, para) which differ by reason of the different relative position of the two substituting groups. This will be evident from the structural formulae, as now written:



The long controversies which ended about 1860 in the triumph of Avogadro's hypothesis and the vindication of the atomic theory had been fought out in the organic field, and had culminated in the establishment of the valence theory as the guiding principle in that branch of the science. This gave, perhaps, to organic chemistry a somewhat exaggerated importance—at any rate, the idea that chemical compounds could be visualized as groups of real atoms united by real bonds exerted a remarkable fascination, and young chemists in great numbers began to devote themselves to synthetic studies, attempting on the one hand to prepare from the elements the most complex products of nature, and on the other to make the greatest variety of new combinations in order to find the utmost limits of chemical affinity and molecular stability. The rise of the coal-tar industry and the possibility of preparing from this source so many compounds of practical utility was partly cause and partly effect of this great movement which is going on uninterruptedly at the present day.

If, however, we ask what direct contribution *to the science as a whole* has been made by organic chemistry since 1860 we can hardly give it so high a place. We must rather confess that this branch of the science has lived largely for itself and while it has, during that time, developed a real history of its own which is of fascinating interest to the specialist, its great historical service to chemistry culminated in the work of Williamson, Gerhardt and Kékulé.<sup>11</sup>

(To be concluded)

<sup>11</sup>F. J. Moore, History of Chemistry, p. 212; italics mine.